Chemosphere 79 (2010) 665–671

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Technical Note

The effects of alkaline dosage and Si/Al ratio on the immobilization of heavy metals in municipal solid waste incineration fly ash-based geopolymer

Lei Zheng *, Wei Wang, Yunchun Shi

Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:
Received 16 October 2009
Received in revised form 7 February 2010
Accepted 8 February 2010
Available online 20 March 2010

Keywords:
MSWI fly ash
Geopolymer
Leaching
Kinetic analysis

ABSTRACT

The present research explored the application of geopolymerization for the immobilization and solidification of municipal solid waste incineration (MSWI) fly ash. The influence of alkaline activator dosage and Si/Al molar ratio on the compressive strength and microstructure of MSWI fly ash-based geopolymer was investigated. A geopolymer with the highest strength was identified to occur at an intermediate alkaline activator dosage and Si/Al ratio, and the optimal Na/MSWI fly ash and Si/Al molar ratio was close to 2.8 mol kg^{-1} and 2.0, respectively. IR spectra showed that higher alkaline activator dosage enhanced the structural disruption of the original aluminosilicate phases and a higher degree of polymerization of the geopolymer networks. At low Si/Al ratio, there was an increasing number of tetrahedral Al incorporating into the silicate backbone. As the Na/MSWI fly ash ratio increased, the microstructure changed from containing large macropores to more mesopores and micropores, indicating that more geopolymers are formed. Furthermore, the pore volume distribution of geopolymers was observed to shift to larger pores as the Si/Al ratio increased, which suggests that the soluble silicon content serves to reduce the amount of geopolymers. Heavy metal leaching was successfully elucidated using the first-order reaction/reaction-diffusion model. Combining the results from the microstructure of samples with the kinetic analysis, the immobilization mechanism of Cr, Cu, and Zn was inferred in this study. The methodologies described could provide a powerful set of tools for the systematic evaluation of element release from geopolymers.

1. Introduction

Due to the presence of heavy metals, municipal solid waste incineration (MSWI) fly ash is classified as hazardous waste in many countries, and it needs to be disposed in secure landfills. The disposal of MSWI fly ash should meet the following conditions: (1) powerful fixing capacity for heavy metals, (2) structural stability of the product with comparable strength, and (3) low volume-added rate. The solidification and immobilization of MSWI fly ash through geopolymeric reaction presented in this study could meet the above requirements.

A geopolymeric reaction is a geosynthetic reaction of alumino-silicate minerals in the presence of an alkali solution at low temperatures, in which mechanisms can be expressed in the following reactions (Davidovits, 1994):

$$(Si_2O_5, Al_2O_2)_n + nH_2O \xrightarrow{NaOH,\ KOH} n(OH)_3\text{-Si-O-Al-}(OH)_3$$

$$n(OH)_3\text{-Si-O-Al-}(OH)_3 \xrightarrow{NaOH,\ KOH} (Na,\ K)\left(-\underset{\underset{O}{|}}{Si}-O-\underset{\underset{O}{|}}{Al}-O-\right)_n \quad (1)$$

Eq. (1) only shows the formation of geopolymer with Si/Al = 1, but this ratio differs according to the composition of aluminosilicate and alkaline activator. Normally, geopolymerization involves dissolution, transportation, as well as polycondensation (van Jaarsveld and van Deventer, 1999). It is proposed that the geopolymer gel can diffuse into larger interstitial spaces between the particles. When the gel hardens, the separate alumino-silicate particles are therefore bound together, and the resulting matrix poses good mechanical performance such as compressive strength.

Early research studies have used almost exclusively calcined kaolinite (metakaolinite) as the main source in geopolymerization (Davidovits, 1994). Subsequently, studies were conducted on geopolymers derived from waste materials such as coal fly ash and

* Corresponding author. Tel.: +86 1062772814; fax: +86 1062782910.
E-mail address: zhenl@mails.tsinghua.edu.cn (L. Zheng).

0045-6535/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2010.02.018

furnace slag, and many of these studies utilized kaolinite, metakaolinite, or other natural aluminosilicate materials in addition to waste to synthesize geopolymers (van Jaarsveld and van Deventer, 1999; Bankowski et al., 2004; Li and Liu, 2007). To date, there are few published literatures dealing with MSWI fly ash-based geopolymer. The present study investigates the geopolymer derived from MSWI fly ash without the addition of other natural aluminosilicate, aiming at a low volume-added rate.

Geopolymers have already been used to stabilize heavy metals (Van Jaarsveld et al., 1997). The exact mechanism by which heavy metal immobilization occurs is not fully understood, and it is thought to be caused by the following routes: (1) metal ions are taken into the geopolymer network; (2) metal ions are bound into the structure for charge balancing roles; and (3) a precipitate containing heavy metals is physically encapsulated. The evaluation of the element release behavior of heavy metals from geopolymer is critical for assisting in the understanding of immobilization mechanism. Most leaching tests in published researches were designed to assess the stability in a utilization/disposal scenario, among which the standard USEPA toxic characteristic leaching procedure method or its modification test was often used (van Jaarsveld and van Deventer, 1999; Bankowski et al., 2004; Phair et al., 2004; Xu et al., 2006; Zhang et al., 2006). Some static leaching tests with acid or salty solution were also conducted (Zhang et al., 2008). However, the systematic evaluation of the leaching process, with focus on reaction kinetics, is limited.

The role played by alkaline activator dosage and Si/Al has been acknowledged as having dominant impacts on geopolymerization (Sindhunata et al., 2006; Duxson et al., 2007). The present work investigates the geopolymerization of MSWI fly ash to determine the effects of alkaline activator dosage and Si/Al molar ratio on the compressive strength and microstructure of geopolymers. A static monolithic leaching test was performed for cylinder geopolymer, and kinetic calculations using the first-order reaction/diffusion model were performed to gain a better understanding of the leaching process. These methods were used to provide an integrated synopsis on the solidification and immobilization mechanisms of MSWI fly ash-based geopolymerization.

2. Experimental

2.1. Materials

Fly ash was sampled from a MSW incineration plant in East China, which had three sets of 350 t d^{-1} stoker furnace. In each furnace, a semi-dry lime scrubbing system and fabric bag filter precipitator are applied. Fly ash used in this paper was sampled from the ash exhaust of the fabric bag filter precipitator. Major element analysis was performed by X-ray fluorescence spectrometry (Shimadzu Lab Center XRF-1700, Japan). The concentration of trace elements was analyzed after the sample was microwave digested with acid according to a previously published protocol (Mester et al., 1999). Acid mixture was as method 3 in Mester's study but a double ratio of acid to fly ash was used. The digested solution was filtered through a 0.45 μm membrane, and the element concentrations were then determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Perkin2Elmer Elan 6000, USA). Fly ash contained large amounts of CaO, Cl, SiO_2, SO_3, Al_2O_3, and Na_2O, and the major heavy metals identified were Zn, Cu, Pb, Cr, Ni, and Cd (see Table 1). Distilled water and analytical grade NaOH and Na_2SiO_3 were used in all experiments.

Table 1
Chemical composition of MSWI fly ash.

Major components	Value	Trace elements	Value (mg kg^{-1})
CaO (wt.%)	28.8	Zn	3692
Cl (wt.%)	19.6	Cu	2817
SiO_2 (wt.%)	15.4	Pb	826
SO_3 (wt.%)	8.7	Cd	103
Al_2O_3 (wt.%)	7.2	Ni	78
Na_2O (wt.%)	6.5		
K_2O (wt.%)	4.3		
Fe_2O_3 (wt.%)	3.6		
MgO (wt.%)	2.2		
Cr (ppm)	1785		
Others	3.5		

2.2. Synthesis of geopolymer

The water-to-fly-ash mass ratio of all batches was fixed at 0.25. Due to our preliminary study, this ratio should higher than 0.18 to ensure easily de-molding, but also should lesser than 0.3 to prevent water exclusion during uniaxial pressing (see details later). Thus 0.25 was chosen in our study. NaOH (15 M) and Na_2SiO_3 (3 M) solutions were prepared and were sealed to avoid carbonation and left to cool to room temperature overnight. The MSWI fly ash (12 g) was first mixed with designed amount of alkali activator. The mixtures were then compacted by uniaxial pressing in a mold (Φ 20 mm, H 40 mm) by 6 MPa compaction pressure. The demolded specimens were subsequently cured at room temperature until the other tests were carried out. Compressive strength testing was performed at the age of 7 d.

The influence of alkaline activator dosage and Si/Al on compressive strength was investigated. For the Na/MSWI fly ash and Si/Al ratios specified in the present investigation, Si and Al were contributed by both the alkaline activator solution and the MSWI fly ash, with Na being counted only from the alkaline activator solutions. Table 2 is a summary of the compositions of all matrices. Series 1 was conducted to optimize Si/Al ratio for strength performance at a fixed Na/MSWI fly ash ratio (1.7 mol kg^{-1}). Series 2 was designed to optimize Na/MSWI fly ash ratio at a fixed Si/Al ratio (equal to an optimal Si/Al value determined through series 1). Similarly, series 3 and 4 were carried out successively to optimize Na/MSWI fly ash and Si/Al ratio for strength performance. Series 5 in Table 2 was used to assess the effect of compositional ratio on the microstructure of geopolymers. In the paper, 'P-a-b' ('a' and 'b' are numbers) was used to denote geopolymer synthesized with the following compositions: Na/MSWI fly ash = a mol kg^{-1} and Si/Al = b mol mol^{-1}.

2.3. Analysis methods

Compressive strength testing was performed using 20 mm diameter cylinders with a 1:2 diameter-to-length ratio. Five cylinders of each sample were tested, averaging the experimental values obtained. An Amsler FM 2750 compressive strength testing apparatus was used. The IR spectra were recorded on a PerkinElmer spectrometer model 1430 in 4000–500 cm^{-1} range using KBr as dispersant. A mineralogical analysis was conducted by X-ray powder diffraction (XRD) (Rigaku D/MAX-RB, Japan). The setting conditions for the XRD were as follows: Cu Kα radiation, 40 keV accelerating voltage, 80 mA current, 5–70° 2θ scanning range, 0.02° step, and 6° min^{-1} scan speed. The specific surface area and the pore distribution were measured by the N_2 gas adsorption BET and BJH method (ASAP 2010, Micromeritics, USA), and mercury intrusion pore distribution, density, and porosity were determined by mercury intrusion porosimetry (AUTOSCAN-33, USA).

2.4. Leaching test and model

Static monolithic leaching tests were conducted for the series 5 samples. The cylinder sample was statically leached with nitric